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Synthesis and Complexing Ability of Hyperbranched Polyester Polyols Containing Carboxylic Acid Fragments

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Abstract—New hyperbranched polyester polycarboxylic acids containing terminal propanoic and acrylic acid fragments have been synthesized. According to the IR spectral data, the complexation of polydentate hyperbranched polyester polycarboxylic acids with Co(II), Ni(II), and Cu(II) ions involves chelation and bidentate bridging coordination by the terminal carboxy groups. All Co(II), Ni(II), and Cu(II) complexes with the obtained polyester polypropanoic acids are characterized by octahedral geometry of the coordination entity (MO_6). The Co(II), Ni(II), and Cu(II) complexes with polyester polyacrylic acids have tetrahedral configuration of the coordination entity (MO_4).

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Synthesis of biologically active compounds with desired properties on the basis of functionalized hyperbranched polymers is an important problem of modern fundamental and applied chemistry [1, 2].

We previously demonstrated the possibility of using carboxylic derivatives of hyperbranched polyester polyols for drug binding and targeted delivery [3] and synthesis of composite metal nanoparticles [4]; furthermore, antimycotic activity of some derivatives, metal complexes [5], and nanoparticles stabilized by these derivatives [6] has been revealed. Variation of the generation of hyperbranched polyester polyols, nature and amount of carboxylic acid fragments, and metal ions makes it possible to obtain new derivatives with practically useful properties.

Therefore, the goal of the present work was to synthesize new hyperbranched polyester polyacids with terminal carboxylic acid fragments and their complexes with 3*d* metal ions, namely cobalt(II), nickel(II), and copper(II). Hyperbranched polyester polyol **H30** [3] containing 32 terminal hydroxy groups was chosen as the initial modifiable platform. Its functionalization afforded polyester polypropanoic acid $\mathbf{L}^{I}$ and polyester polyacrylic acids $\mathbf{L}^{II}$ and $\mathbf{L}^{III}$ (Scheme 1).

The ^{1}H NMR spectrum of $\mathbf{L}^{I}$ displayed additional signals at δ 2.62 ppm due to methylene protons of the $OC(O)CH_2CH_2COOH$ fragment, and protons of the acylated CH_2OR groups resonated as two doublets at δ 4.2–4.5 ppm. The signal of unreacted CH_2OH groups was located at δ 3.69 ppm. Analysis of the ^{1}H NMR spectra of $\mathbf{L}^{II}$ (Fig. 1) and $\mathbf{L}^{III}$ showed that the CH=CH bonds have *cis* configuration (δ 6.41 ppm); the double-bonded carbon atoms gave rise to doublets at δ_C 130.1 and 131.7 ppm in the ^{13}C NMR spectra. As in the ^{1}H NMR spectrum of $\mathbf{L}^{I}$, protons of the CH_2OR fragments of $\mathbf{L}^{II}$ and $\mathbf{L}^{III}$ resonated as two doublets at δ 4.2–4.5 ppm.

According to the pH-potentiometric titration [7] and NMR data, the degree of functionalization of $\mathbf{L}^{I}$ and $\mathbf{L}^{III}$ was 69% (22 of the 32 possible carboxy groups were introduced), and the degree of functionalization of $\mathbf{L}^{II}$ was 56.25% (18 of the 32 possible COOH groups).

The IR spectrum of the initial polyester polyol was described in [8]. The IR spectrum of $\mathbf{L}^{I}$ displayed a significant increase in intensity and shift of the carbonyl stretching band at 1730 cm^{-1} due to hydrogen bond formation. In addition, an absorption band at 2752 cm^{-1} appeared due to stretching vibrations of the OH groups in the terminal carboxylic acid fragments. In the IR spectra of third-generation polyester polyacrylic acids $\mathbf{L}^{II}$ and $\mathbf{L}^{III}$, we observed a new strong band at 1640 or 1641 cm^{-1}, respectively, which was assigned to stretching vibrations of the C=C double bond in the OC(O)CH=CHCOOH fragments. The